# Electronic Supplementary Information

## A novel fluorescent aptasensor for ultrasensitive and selective detection of acetamiprid pesticide based on inner filter effect between gold nanoparticles and carbon dots

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## Materials and methods

### Quantum Yield Calculations

The quantum yield (Φ) of the carbon dots (CDs) was calculated using quinine sulfate as reference[1, 2]. Briefly, the quinine sulfate (literature Φ = 0.54) was dissolved in 0.1 M $H_2SO_4$ (refractive index (η) of 1.33) while the CDs was dissolved in water (η = 1.33). Using quinine sulfate as a reference, the integrated fluorescence intensities and the absorbance values (less than 0.05) of the prepared CDs and quinine sulfate were measured.

The quantum yield was calculated using the below equation:

$$\Phi = \Phi_R \times \frac{\mathrm{I}}{\mathrm{I}_R} \times \frac{\mathrm{A}_R}{\mathrm{A}} \times \frac{\eta^2}{\eta_R^2}$$

Where Φ, I, η refer to the quantum yield, the measured integrated emission intensity and refractive index, respectively. A is the absorbance values and the subscript R is the reference fluorescent substance of known quantum yield. The quantum yield for the as-prepared CDs is calculated to be 64.5%.

**Preparation of AuNPs**

Citrate-coated AuNPs (CC-AuNPs) were obtained by classical citrate reduction of $HAuCl_4$ according to our previous reports[3]. In Briefly, 10 mL of 38.8 mM sodium citrate solution was rapidly added to a boiling 100 mL of 1.0 mM $HAuCl_4$ solution under vigorous stirring. The mixed solution was boiled for 15 min and further stirred for another 15 min then cooled to room temperature and filtered using an ultrafiltration membrane (250 nm aperture). In the case of cysteamine-stabilized AuNPs (CS-AuNPs), 1.2 mL of 213 mM cysteamine and 1.42 mM $HAuCl_4$ were mixed, and then the mixture was blended under ambient temperature for 20 min. Subsequently, 30 mL of 10 mM $NaBH_4$ was added to the above solution, and the mixture was stirred for another 25 min at room temperature in the dark[4]. As for unmodified AuNPs (umAuNPs), according to the borohydride reduction method, 1.5 mL of 29.43 mM $HAuCl_4$ solution was diluted with 118.5 mL bi-distilled water. Afterward, 3 mL of 264.34 mM $NaBH_4$ solution were added dropwise under vigorous stirring. The resulting wine-red colloidal solution was further stirred for 30 min and then left undisturbed overnight[5]. All the AuNPs solutions were stored in a refrigerator at 4 °C, and their amounts were determined according to Bouguer–Lambert–Beer law: A=kcd (where A is the absorption, k is the molar extinction coefficient, c is the sample concentration and d is the optical path length). $c=A_{450}/\varepsilon_{450}$, where c is in mol per litre and the absorption A at 450 nm for a standard path length of 1 cm is used.

**The operating parameters of LC-MS**

Compare with previous literature[6], the liquid chromatography-mass spectrometry (LC-MS) analysis of acetamiprid was carried out on a Shimadzu (Tokyo, Japan) 20 AD-XR LC system (Shimadzu Corporation, Kyoto, Japan). The column was an Agilent Eclipse XDB-C18 column (4.6 mm × 150 mm, 5 μm particle size, Agilent California, USA). The LC operating parameters were as follows: the column temperature was 40 °C, and the flow rate was 0.8 mL/min with an injection volume of 5 μL. The mobile phase was a mixture of a 0.1% formic acid aqueous solution (A) and acetonitrile (B). The chromatographic gradient started at 10% B (0.0–0.5 min), increased to 95% B (0.5–7.5 min), held at 95% B (7.5–8.0 min), decreased to 10% B (8.0–8.01 min), and maintained at 10% B (8.01–10.0 min). The retention times of acetamiprid were approximately 3.64 min.

An Applied Biosystems Sciex API 4000Q Trap quadrupole mass spectrometer equipped with an Ion Source Turbo Spray unit (Thermo Fisher Scientific, Waltham, USA) was applied to quantify the acetamiprid pesticide. The curtain gas, nebulizer gas and collision gas were all nitrogen. The electrospray ionization (ESI) source-dependent parameter settings were as follows: declustering potential, 77.1 V; curtain gas pressure, 25.0 kPa; ion spray voltage, 5500 V; ion source temperature, 600 °C; ion source gas 1 pressure, 55.0 kPa; and ion source gas 2 pressure, 55.0 kPa. The analysis of acetamiprid was performed in positive mode using multiple reaction monitoring (MRM) with two mass transitions. The m/z 223.1→126.0 transition was set as the quantification transition, and the m/z 223.1→56.1 transition was set as the confirmation transition. The collision energy was set at 27 and 35 V for product ions 126.0 and 56.1, respectively.

**Table S1** Comparison of fluorescent quantum yields of the previously reported carbon dots synthesized by hydrothermal method

| CD | Materials | The range of size(nm) | The surface potential (mV) | Quantum yield (%) | Ref |
|---|---|---|---|---|---|
| 1 | Citric acid anhydrous + ethylenediamine + deionized water | 2-6 | -7.2 | 65.5 | 7 |
| 2 | Citric acid + ethylenediamine + deionized water | 2-5 | -6.2 | 76 | 8 |
| 3 | Aspartic acid + deionized water | 3.0-4.5 | -5.9 | 41.3 | 9 |
| 4 | Citric acid + $(NH_4)_2HPO_4$ + deionized water | 1.5-4 | -4.8 | 59 | 10 |
| 5 | Citric acid + ethylenediamine + deionized water | 3-7 | - 2.6 | 64.5 | This work |

**Table S2** Comparison with earlier aptamers-based methods for acetamiprid detection

| Methods | Transduction principle | Linear range (μg· $L^{-1}$) | LOD (μg· $L^{-1}$) | Ref |
|---|---|---|---|---|
| Colorimetry | The peroxidase activity of AuNPs is controlled by the specific binding of the target and aptamers to catalyze TMB | 100-1.0 × $10^4$ | 100 | 11 |
| | The enhanced peroxidase activity of AuNPs based on the specific binding of the target and aptamers to catalyze ABTS | 10-50 | 1.02 | 12 |
| | Aggregation of AuNPs based on the specific binding of the target and aptamers in NaCl solution | 17-1.7 × $10^3$ | 1.1 | 13 |
| Electrochemistry | Signal amplification utilizing AuNPs as the support for aptamer immobilization | 56-446 | 19 | 14 |
| | A decrease of the enhanced photocurrent produced by the electron donor of quercetin based on the specific binding of the target and aptamers | 0.1-178 | 0.04 | 15 |
| Chemiluminescence | Aggregation of AuNPs based on the high binding of the target and aptamers which amplifies the chemiluminescence signal in the presence of luminol and $H_2O_2$ | None | 0.01 | 16 |
| Fluorescence | Release of the fluorescein-labeled complementary strand of the aptamer (CS) from the aptamer/CS conjugate based on the specific binding of the target and aptamers | 0.09-156 | 0.03 | 17 |
| | Aggregation of AuNPs based on the specific binding of the target and aptamers and turns on the fluorescence of CdTe QDs | 11-223 | 1.6 | 18 |
| | Reduce the fluorescence intensity of probe based on the dissociation of cDNA-UCNPs from aptamer-MNPs through the specific binding of the target and aptamers | 0.89-114.18 | 0.65 | 19 |
| | Release fluorescent signal from the internal filter effect quenching of dispersed AuNPs toward CDs based on the specific binding of the target and aptamers | 5-100 | 1.08 | This work |

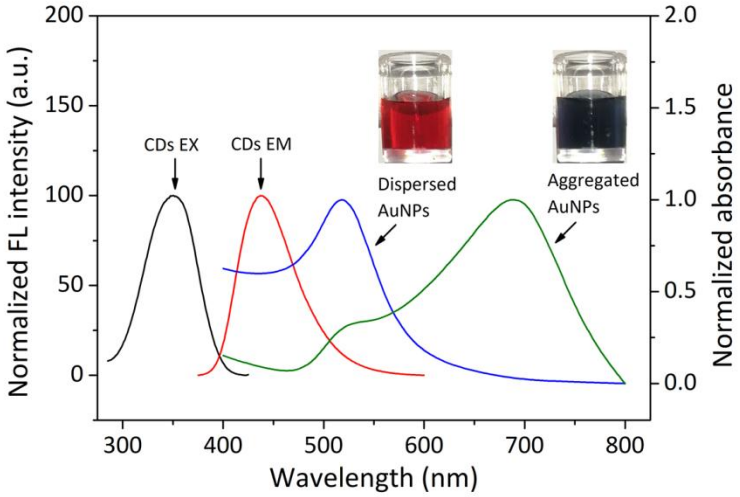


**Fig. S1** Normalized excitation and emission spectra of CDs integrated with the color and normalized absorption spectra of dispersed and aggregated CC-AuNPs

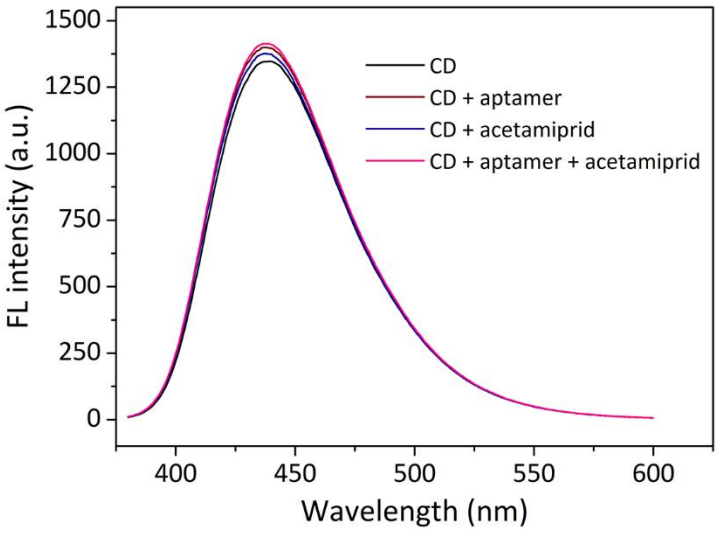


**Fig. S2** Emission spectra of the prepared CDs treated with S-18 aptamer or acetamiprid. The concentrations of CDs, acetamiprid and S-18 aptamer were 0.2 mg·mL$^{-1}$, 1 mg·L$^{-1}$ and 25 nM, respectively. The excitation and emission wavelength were 350 nm and 437 nm.

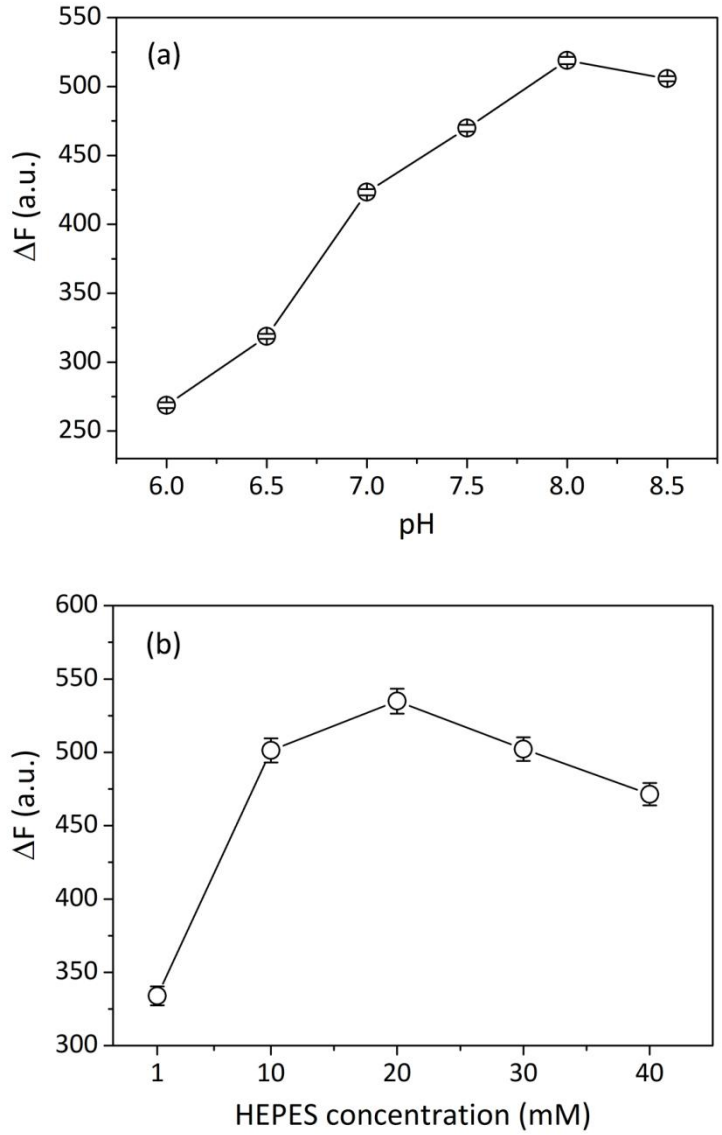


**Fig. S3** Effect of pH (a) and HEPES concentration (b) on the aptasensor. The concentrations of CDs, CC-AuNPs and S-18 aptamer were 0.2 mg·mL$^{-1}$, 3.2 nM and 25 nM, respectively. The excitation and emission wavelength were 350 nm and 437 nm.

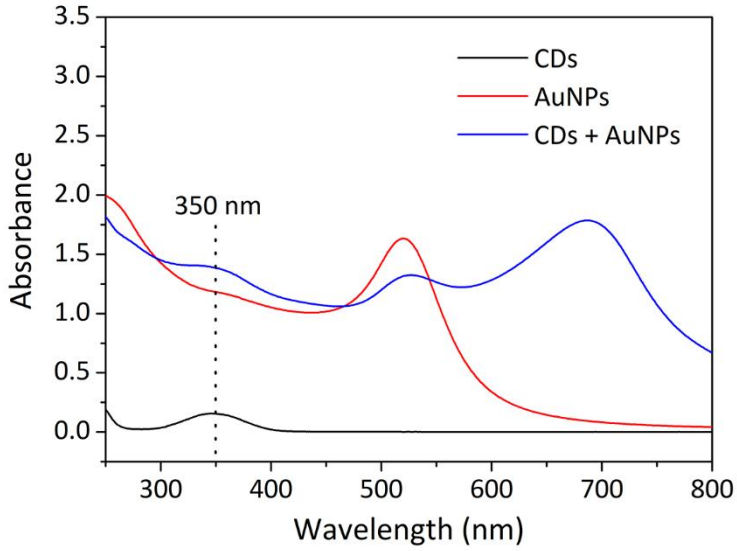


**Fig. S4** UV-vis spectra of the prepared CDs in the absence and presence of CC-AuNPs. The concentrations of CDs and CC-AuNPs were 0.2 μg·mL$^{-1}$ and 8 nM, respectively.

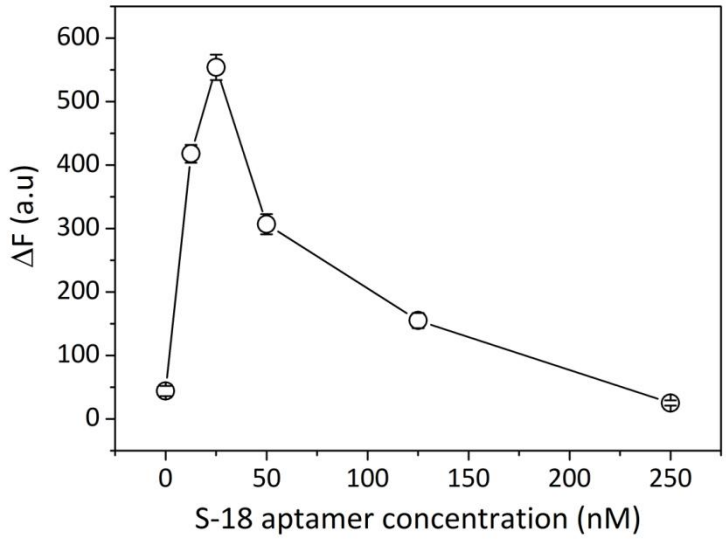


**Fig. S5** Effect of S-18 aptamer concentration on the fluorescent aptasensor. The amounts of CDs and CC-AuNPs were 0.2 mg·mL$^{-1}$ and 3.2 nM. The excitation and emission wavelength were 350 nm and 437 nm, respectively.

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